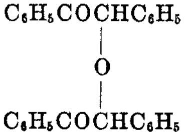
[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS AND THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE REACTION OF PHENYLBENZOYLDIAZOMETHANE WITH BENZOIN[1]

DAVID Y. CURTIN[2] AND WILLIAM R. PROOPS

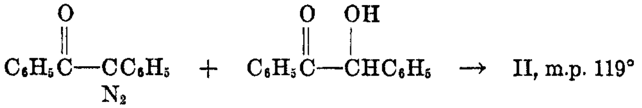
Received October 30, 1953

In the course of an investigation of possible methods of synthesis of didesyl ether (I) the reaction of benzoin with phenylbenzoyldiazomethane in the presence of boron trifluoride etherate was examined. This method had been developed by Newman and Beal (1) for the synthesis of other α-alkoxy ketones. The product (II), m.p. 191°, was found to have the correct analysis and molecular weight for the expected keto ether (I). The infrared absorption spectrum (Fig. 1) of II, however, either in a Nujol mull or in carbon disulfide, failed to show the presence of a carbonyl group. Furthermore, the ultraviolet spectrum (Fig. 2) was that to be expected of a molecule containing only unconjugated phenyls and indicated specifically that the functional group, $C_6H_5C{=}O$ was absent (2).



$$\begin{array}{c} C_6H_5COCHC_6H_5 \\ | \\ O \\ | \\ C_6H_5COCHC_6H_5 \end{array}$$

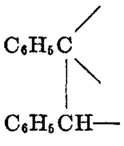
I



$$C_6H_5\overset{O}{\overset{\|}{C}}-\underset{N_2}{C}C_6H_5 + C_6H_5\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}}HC_6H_5 \rightarrow \text{II, m.p. } 119^\circ$$

Compound II was stable toward refluxing ethanolic potassium hydroxide and the spectral evidence for the absence of a carbonyl function was confirmed by the fact that attempts to convert it to an oxime in basic solution led only to the recovery of starting material.

On the other hand, II reacted readily with dilute ethanolic hydrochloric acid to give approximately two moles of benzoin per mole of II employed. Furthermore, it reacted with 2,4-dinitrophenylhydrazine hydrochloride to give approximately two moles of benzil 2,4-dinitrophenylosazone.



A

---

[1] Taken from a thesis submitted by William R. Proops to Columbia University in partial fulfillment of the requirements for the Ph. D. degree.

[2] Department of Chemistry, University of Illinois.

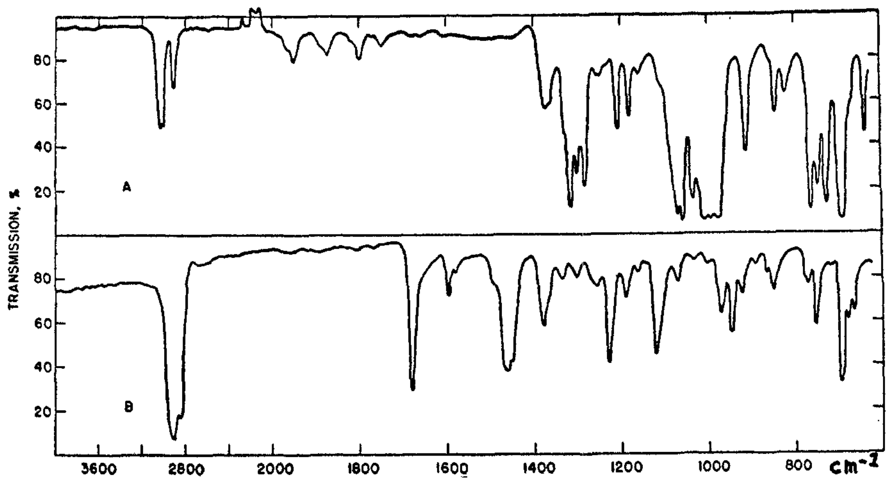
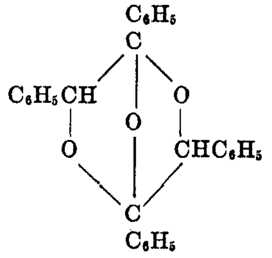
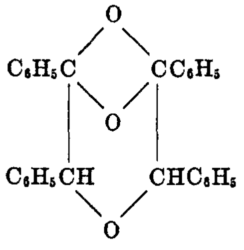


Fig. 1. Infrared Absorption Spectra. Curve A, Compound II ($C_{28}H_{22}O_3$) in CS_2. Curve B, Didesyl ether in Nujol.

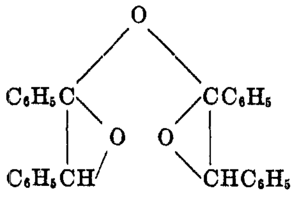
The presence of a functional group which, although not a carbonyl or hydroxyl group, is readily hydrolyzed to such groups in the presence of dilute acid and is stable to base suggests an acetal or ketal. The ready formation of two moles of benzoin from one mole of II suggests strongly that II consists of two identical fragments (A) attached to each other through three oxygens. The three possible structures which meet these requirements are shown below.



(B)



(C)



(D)

Although it has not been possible to devise a rigorous chemical method for eliminating structures (C) and (D), strong evidence against them and support for (B) can be advanced.

The hydrolysis of II to benzoin on mild treatment with ethanolic hydrochloric acid appears to exclude structure (C) since a substance with this structure should give didesyl ether (I) which, as will be shown later, can be hydrolyzed to benzoin only under considerably more rigorous conditions and in much poorer yield.

An excellent model (III) for structure (D) has been prepared by Stevens, Weiner, and Freeman (3) and shown to react with 0.5 *M* sodium methoxide in methanol at room temperature, and, further, to be rearranged to benzoin methyl

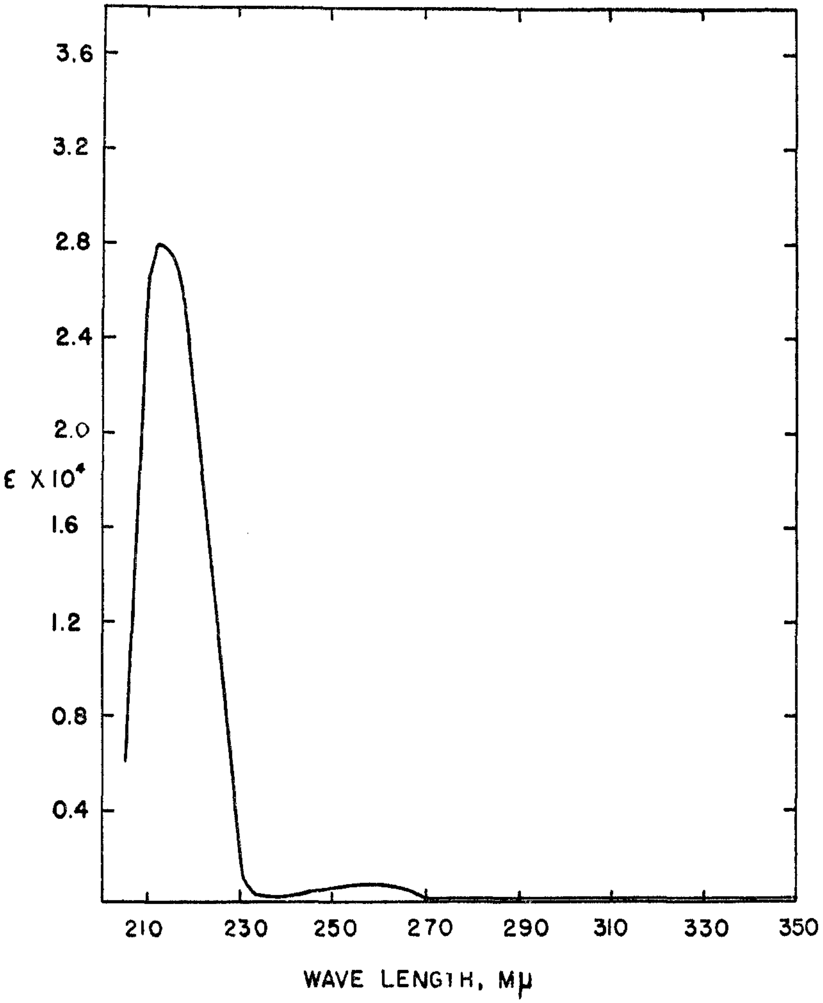
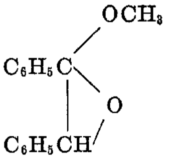


FIG. 2. ULTRAVIOLET ABSORPTION SPECTRUM. Compound II ($C_{28}H_{22}O_3$) in 95% ethyl alcohol.

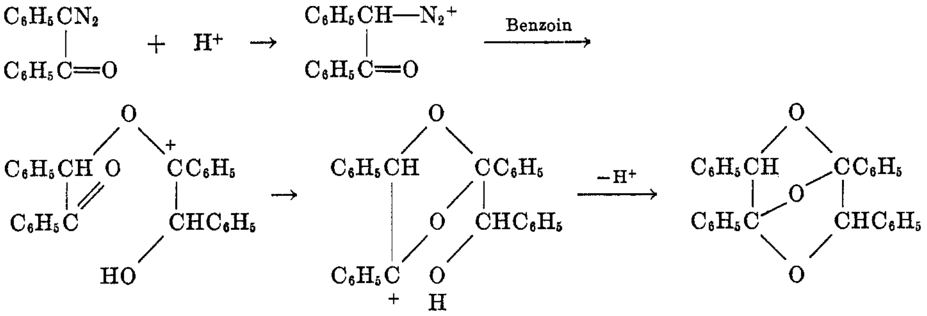
ether by treatment with magnesium bromide in ether. It seems quite improbable, therefore, that II would show the observed stability toward boiling ethanolic potassium hydroxide and toward boron trifluoride (to which it was exposed during its formation) if it possessed structure (D).



III

Compound II is, therefore, in all probability, 2,5-oxido-2,3,5,6-tetraphenyldioxane (B).

It may be noted that the formation of a substance with this structure is readily explained by the path below.



II

Madelung and Oberwegner (4) have previously reported the synthesis of two substances (m.p. 154° and 198°) which were considered to be the two possible racemic 2,5-oxido-2,3,5,6-tetraphenyldioxanes. Although their isomer, m.p. 198°, might be suspected of being identical with II (m.p. 191°) it was reported to show different chemical behavior. For example, either the isomer m.p. 198° or that m.p. 154° on treatment with potassium hydroxide in ethanol was converted to benzilic acid and benzoin whereas II did not react. It appears that the structures of the two isomers of Madelung and Oberwegner require further investigation.

When the reaction of benzoin with phenylbenzoyldiazomethane was carried out without added boron trifluoride, the only product obtained was benzoin diphenylacetate probably arising from the reaction of benzoin with diphenylketene initially formed.

It had been reported by Madelung and Oberwegner (4) that benzoin reacts with perchloric acid and sulfuric acid in chloroform to give one of the diastereoisomeric racemates of (I). The evidence for the structure of I was that it formed a dioxime and reacted with ethanolic potassium hydroxide to give desoxybenzoin and benzil, although no yields or other details were given for the latter reaction. Because of the unorthodox synthesis of I and the lack of detail concerning its cleavage, it was desired to repeat its synthesis and to study its behavior toward base. The procedure of Madelung and Oberwegner was repeated and found to give I in 20% yield. The structure which had been assigned was confirmed by the infrared spectrum which showed a strong carbonyl band at 1685 cm^{-1}. When I was allowed to react with hydrochloric acid in ethanol under reflux, benzoin (25% yield) and benzil (47%) were the only products obtained. Madelung and Oberwegner had reported without experimental detail that I was cleaved to benzil and desoxybenzoin by dilute acid. Compound I reacted very readily with base. Even aqueous sodium carbonate converted it to benzil (54%) and desoxybenzoin (65%). Madelung and Oberwegner had reported a similar cleavage with potassium hydroxide in ethanol for 24 hours (concentration unspecified). None of the carbinol to be expected from an oxygen-to-carbon rearrangement was observed. Desyl trityl ether has been found previously to undergo a similar cleavage (5). In the present case the possibility that I initially rearranged to α-desylbenzoin which then underwent a reverse aldol reaction to give the cleavage products observed is not excluded. Hauser and Kantor (6) however, were able to show that dibenzyl ether undergoes an analogous rearrangement with potassium amide to benzylphenylcarbinol and elimination to benzaldehyde and toluene and that neither pair of products is intermediate in the formation of the other.

EXPERIMENTAL[3]

Reaction of phenylbenzoyldiazomethane with benzoin. Formation of II. To a solution of 16 g. (0.075 mole) of benzoin and 8.0 g. (0.036 mole) of phenylbenzoyldiazomethane (7), m.p. 77–79°, in 320 ml. of dry benzene was added 0.8 g. of boron trifluoride etherate. After 30 minutes at 32°, 90% of the theoretical amount of nitrogen had been evolved and the color of the solution had changed from red to yellow. The reaction mixture was decomposed with 200 ml. of 10% sodium carbonate solution, 200 ml. more of benzene was added, and the benzene solution was washed with 200 ml. of 10% sodium carbonate, dried over magnesium sulfate, and evaporated to a volume of 50 ml. Benzoin (12 g., 0.057 mole), m.p. 127–129°, which had crystallized was removed by filtration. The filtrate was evaporated further under 15 mm. pressure on a steam-bath and 30 ml. of methanol was added. Crystals of II were filtered, washed with 10 ml. of hot ethanol, and recrystallized twice from 1:5 benzene-hexane to give 1.3 g. (0.0032 mole or 17% based on unrecovered benzoin) m.p. 189–190°. Further recrystallization raised the m.p. to 190–191°. The molecular weight was determined in camphor.

Anal. Calc'd for $C_{28}H_{22}O_3$: C, 82.7; H, 5.5; M.W., 406.
Found: C, 83.0; H, 5.6; M.W. 426, 433.

The infrared absorption spectrum of a 10% solution of II in carbon disulfide is given in Fig. 1, Curve A. The ultraviolet spectrum showed maxima at 212 mμ and 257 mμ with extinction coefficients of 28,000 and 810, respectively. These maxima agree well with the spectrum to be expected of a molecule containing four unconjugated benzene rings since benzene has maxima at 200 mμ and 255 mμ with extinction coefficients of 4,470 and 220, respectively (2).

Reaction of II *with hydrochloric acid.* A suspension of 0.25 g. (0.00062 mole) of II in 25 ml. of ethanol containing 0.5 ml. of concentrated hydrochloric acid was heated under reflux for 15 minutes after which time the II had dissolved. The solution was then poured into 175 ml. of water, cooled, and filtered to give 0.22 g. (0.0010 mole, 84%) of benzoin, m.p. 130–132°. Mixture m.p.'s with authentic benzoin gave no depression.

Reaction of II *with 2,4-dinitrophenylhydrazine.* II (0.25 g., 0.00062 mole) was heated under reflux for 12 hours with 1.0 g. (0.0050 mole) of 2,4-dinitrophenylhydrazine in 35 ml. of ethanol containing 2 ml. of concentrated hydrochloric acid. The benzil 2,4-dinitrophenylosazone (0.64 g., 0.0011 mole, 92%) was collected; m.p. 317–318°. A mixture m.p. showed no depression.

Treatment of II *with hydroxylamine and with potassium hydroxide.* When 0.30 g. of II was

---

[3] All melting points are corrected. *Microanalyses* were carried out by the Schwarzkopf Microanalytical Laboratory, Elmhurst, Long Island; and by Miss E. Davis at the University of Illinois. *Infrared spectra* were measured by Miss H. Miklas and Mrs. R. F. Hill with a Perkin-Elmer double beam spectrophotometer, Model 21, with NaCl cells. *Ultraviolet spectra* were determined by Mr. H. Birch and Miss E. Richards using a Cary recording spectrophotometer, Model 11, with a 1-cm. quartz cell.

heated under reflux with 0.3 g. of hydroxylamine hydrochloride and 1.2 g. of potassium hydroxide in 7 ml. of ethanol for 1 day and the reaction mixture was poured into 75 ml. of water, 0.28 g. (93%) of starting material, m.p. and mixture m.p. with authentic II, 189–190°, was recovered.

When II (0.50 g.) was treated under reflux for 1 day with 75 ml. of ethanol saturated with potassium hydroxide, 94% of the starting material was recovered as shown by m.p. and mixture m.p., 187–189°.

Uncatalyzed reaction of benzoin and phenylbenzoyldiazomethane, Benzoin diphenylacetate. A solution of 6.0 g. (0.028 mole) of benzoin and 3.0 g. (0.014 mole) of phenylbenzoyldiazomethane in 100 ml. of dry benzene was refluxed for four hours. Nitrogen evolution began almost immediately and the color of the solution changed from red to light yellow. The benzene was removed under reduced pressure on a steam-bath and the residue was washed four times with 25-ml. portions of hot ethanol. The remaining solid was crystallized from benzene-hexane to give 4.2 g. (0.010 mole, 71%) of benzoic diphenylacetate, m.p. 156.5–157.5°, reported 155° (4). An infrared spectrum in Nujol showed the ester carbonyl at 1742 cm.$^{-1}$ and the ketonic at 1685 cm.$^{-1}$.

Didesyl ether (I) was prepared in a yield of 18% according to the procedure of Madelung and Oberwegner (4). The infrared spectrum is shown in Curve B of Fig. 1.

When 1.00 g. of I was heated under reflux for 14 hours with 25 ml. of ethanol containing 7 ml. of concentrated hydrochloric acid, 0.25 g. (25%) of benzoin, m.p. 126–129°, and 0.04 g. (4%) of benzil were isolated by pouring the solution into 100 ml. of water and extraction with ether.

Reaction of didesyl ether (I) *with aqueous sodium carbonate.* A suspension of 1.00 g. (0.00246 mole) of I was refluxed with stirring for 36 hours with 100 ml. of 10% sodium carbonate. The suspended yellow oil was extracted with ether. Removal of the ether and crystallization of the residue from methanol gave 0.28 g. (0.00013 mole, 54% yield) of benzil, m.p. 90–92°. A mixture m.p. with authentic benzil showed no depression. Evaporation of the filtrate and chromatography of the residue on alumina gave 0.31 g. (0.0016 mole, 64% yield) of desoxybenzoin, m.p. and mixture m.p. 51–53°.

SUMMARY

Phenylbenzoyldiazomethane has been found to react with benzoin in the presence of boron trifluoride to give a substance which available evidence indicates is one of the two possible racemic 2,5-oxido-2,3,5,6-tetraphenyldioxanes. When the reaction is carried out in the absence of boron trifluoride the product is benzoin diphenylacetate.

The Madelung and Oberwegner synthesis of didesyl ether from benzoin and perchloric and sulfuric acids has been repeated. Didesyl ether reacts even with aqueous sodium carbonate to give benzil and desoxybenzoin.

URBANA, ILLINOIS
NEW YORK, 27, N. Y.

REFERENCES

(1) NEWMAN AND BEAL, *J. Am. Chem. Soc.*, **72**, 5161 (1950).
(2) BRAUDE, *Ann. Repts. on Prog. Chem.* (*Chem. Soc. London*), **42**, 123 (1945).
(3) STEVENS, WEINER, AND FREEMAN, *J. Am. Chem. Soc.*, **75**, 3977 (1953).
(4) MADELUNG AND OBERWEGNER, *Ann.*, **526**, 195 (1936).
(5) CURTIN AND LESKOWITZ, *J. Am. Chem. Soc.*, **73**, 2633 (1951).
(6) HAUSER AND KANTOR, *J. Am. Chem. Soc.*, **73**, 1437 (1951).
(7) NENITEZESCU AND SOLOMONICA, *Org. Syntheses*, Coll. Vol. II, 496 (1943).